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230Th-234U Age-Dating Uranium by Mass Spectrometry

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Disclaimer

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SAMPLE DISSOLUTION AND PURIFICATION FOR ^{230}TH-^{234}U AGE-DATING

1 SCOPE AND APPLICATION

This is the standard operating procedure used by the Isotope Ratio Mass Spectrometry Group of the Chemical Sciences Division at LLNL for the preparation of a sample of uranium oxide or uranium metal for ^{230}Th-^{234}U age-dating. The method described here includes the dissolution of a sample of uranium oxide or uranium metal, preparation of a secondary dilution, spiking of separate aliquots for uranium and thorium isotope dilution measurements, and purification of uranium and thorium aliquots for mass spectrometry. This SOP may be applied to uranium samples of unknown purity as in a nuclear forensic investigation, and also to well-characterized samples such as, for example, U_3O_8 and U-metal certified reference materials.

2 SUMMARY OF METHOD

The sample of uranium is transferred to a quartz or PFA vial, concentrated nitric acid is added and the sample is heated on a hotplate at approximately 100°C for several hours until it dissolves. The sample solution is diluted with water to make the solution approximately 4 M HNO_3 and hydrofluoric acid is added to make it 0.05 M HF. A secondary dilution of the primary uranium solution is prepared. Separate aliquots for uranium and thorium isotope dilution measurements are taken and spiked with ^{233}U and ^{229}Th, respectively. The spiked aliquot for uranium isotope dilution analysis is purified using EiChrom UTEVA resin. The spiked aliquot for thorium isotope dilution analysis is purified by, first, a 1.8 mL AG1x8 resin bed in 9 M HCl on which U adsorbs and Th passes through; second, adsorbing Th on a 1 mL AG1x8 resin bed in 8 M HNO_3 and then eluting it with 9 M HCl followed by 0.1 M HCl + 0.005 M HF; and third, by passing the Th through a final 1.0 mL AG1x8 resin bed in 9 M HCl. The mass spectrometry is performed using the procedure "Th and U Mass Spectrometry for ^{230}Th-^{234}U Age Dating".

3 INTERFERENCES AND LIMITATIONS

3.1 Refractory phases, alloys and precipitates.

Some oxides and most silicate minerals are not soluble in nitric acid alone, and if present in a sample of uranium oxide these will be visible as un-dissolved material. Also, some alloys of uranium metal may not be soluble without the addition of hydrofluoric acid in greater concentrations than the recommended 0.05 M solution. While the addition of hydrofluoric acid may aid dissolution of refractory phases and some alloys, this must be balanced against the likelihood that fluoride precipitates of other elements may form. In any case, presence of un-dissolved material should be called to the attention of the project leader, and the course of action decided upon.

4 APPARATUS AND MATERIALS

4.1 Analytical balance, calibration checked, and set to display at least four decimal places.
4.2 Aluminum foil.
4.3 Flat bottom quartz vials, approximately 1 cm diameter x 8 cm tall.
4.4 PFA Teflon vials with screw tops (e.g., Savillex, 7 mL, 14 mL, 20 mL and 30 mL sizes).
4.5 FEP Teflon bottles (125 mL, 250 mL, 500 mL and 1 L) for reagents.
4.6 FEP Teflon squirt bottles for reagents (250 mL).
4.7 Polyethylene bottles (250 mL, 500 mL, 1 L) for sample dilutions.
4.8 Hot plates and heat lamps.
4.9 Ultrasonic bath.
4.10 Plastic columns with 2 mL bed capacity (e.g., Bio-Rad Poly-Prep).
4.11 Column rack.
4.12 Disposable plastic transfer pipets.
4.13 Variable volume pipettor with tips (e.g., Eppendorf).
4.14 Pen for writing on Teflon (Cryomarker or Staedtler Mars).

5 ANALYTICAL REAGENTS

5.1 ASTM Type II reagent grade water (e.g., Milli-Q water, 18 Mohms)
5.2 Ultra-pure, sub-boiling distilled, concentrated hydrochloric (HCl), nitric (HNO_3), and hydrofluoric (HF) acids (e.g., Seastar Chemicals Inc.)
5.3 HCl, 9 M, prepared by diluting 750 mL concentrated HCl to 1 L with Milli-Q water. Preparation may be scaled to smaller volumes.
5.4 HCl, 5 M, prepared by diluting 417 mL concentrated HCl to 1 L with Milli-Q water. Preparation may be scaled to smaller volumes.
5.5 HCl, 0.1 M, prepared by diluting 8 mL concentrated HCl to 1 L with Milli-Q water. Preparation may be scaled to smaller volumes.
5.6 HCL, 0.1 M + HF, 0.005 M, prepared by diluting 8 mL concentrated HCl plus 0.18 mL concentrated HF to 1 L with Milli-Q water. Preparation may be scaled to smaller volumes.
5.7 HNO_3, 8 M, prepared by diluting 500 mL concentrated HNO_3 to 1 L with Milli-Q water. Preparation may be scaled to smaller volumes.
5.8 HNO_3, 4 M, prepared by diluting 250 mL concentrated HNO_3 to 1 L with Milli-Q water. Preparation may be scaled to smaller volumes.
5.9 HNO_3, 1 M, prepared by diluting 63 mL concentrated HNO_3 to 1 L with Milli-Q water.
5.10 EiChrom UTEVA resin, selective extraction media.
5.11 Bio-Rad AG1x8, 100-200 mesh, chloride form, anion exchange resin
5.12 Lint free wipes (e.g., Texwipe II).
5.13 Isopropyl alcohol (2-propanol) for wipe cleaning.

6 PROCEDURE

6.1 Dissolve uranium sample.

6.1.1 For all samples, prepare a new, cleaned and dried, PFA Teflon screw-top vial with appropriate labels and determine its weight on the analytical balance. A 30 mL vial is appropriate for samples weighing less than 2 grams. Larger teflon jars can be used for larger samples. Reproducible weights on PFA vials and jars can be obtained by weighing them in a tared Al-foil sleeve and using an anti-static device.

6.1.2 Prepare a weighing receptacle. For metal samples, clean a small piece of Al-foil by wiping with a lint-free cloth dampened with isopropyl alcohol. Fold the foil appropriately to fashion a weighing boat for the sample, and tare the boat on the analytical balance. For oxide samples, obtain the weight of a labeled, cleaned and dried, flat bottom quartz vial. For highly dispersible materials, an Al-foil lid can be made for the quartz vial, which should be labeled and weighed with the vial as a unit.

6.1.3 For metal, place the sample on the Al-foil and record its weight. For oxides, transfer the sample to the quartz vial and obtain the weight of the vial plus the sample.

6.1.4 For metal, transfer the sample to the PFA vial and add 5 mL of conc. HNO_3. For oxide powders weighed in quartz vials, quantitatively police the sample into the PFA vial using a few mL of Milli-Q water. Complete the transfer by policing the quartz vial with 5 mL of conc. HNO_3 and adding this to the PFA vial.

6.1.5 Place the cap on the PFA vial but do not tighten, so that any gases formed during digestion are allowed to escape. Place the PFA vial directly on the hotplate and heat at ca. 110°C hotplate setting, with heat-lamp assistance. Samples can be left to dissolve overnight.

6.1.6 Allow the sample to cool and visually assess whether the sample has dissolved completely. See step 3.1.1. Add 1 mL of conc. HNO_3 to the sample.

6.1.7 Add a sufficient quantity of H_2O to the sample in the PFA vial to bring the volume to approximately 25 mL. Add 45 microliters of concentrated hydrofluoric acid to the sample solution to make it 0.05 M HF, cap the vial tightly and shake, warm it on a hotplate and then cool the vial for a few minutes in an ultrasonic bath. Allow the vial to stand for several hours to reach room temperature and then obtain the final weight of the vial with sample solution. This solution is the Primary Solution.

6.2 Prepare Secondary Dilution.

6.2.1 For each sample, calculate the amount of primary solution required to produce a secondary dilution of the desired concentration and volume. The amount transferred should be 0.1 mL or greater, in order to minimize uncertainty associated with weighing. The U concentration of the secondary dilution should be low enough to allow an aliquot of the solution to be spiked with a reasonable quantity of ^{233}U spike that will yield a $^{233}U/^{235}U$ ratio of approximately one. Label a 7 mL or 14 mL PFA Teflon screw-top vial, add approximately 2 mL 4 M HNO_3 to the vial, seal tightly and obtain the weight

of the vial. Transfer the calculated amount of Primary Solution to the vial and weigh again.

6.2.2 Prepare a 250 mL (or other volume, as required) polyethylene bottle with a label, and obtain the empty weight of bottle. Transfer the sample from the PFA vial to bottle, rinse the vial several times with 1 M HNO_3, transferring all rinses to bottle, and then dilute the solution in the bottle to the desired volume with 1 M HNO_3. Obtain the final weight of bottle containing the secondary dilution solution.

6.3 Aliquot and spike samples for U and Th concentration measurement.

6.3.1 Estimate the amount of Secondary Dilution required that will give the desired amount of uranium for analysis. Calculate the amount of ^{233}U spike required for optimal spike/sample ratio for isotope dilution analysis (see 6.2.1). Estimate the amount of Primary Solution required to give desired amount of thorium for analysis. Using estimates of the uranium concentration and a nominal 10 year age, calculate the amount of ^{229}Th spike required for optimal spike/sample ratio for isotope dilution analysis.

6.3.2 For each uranium isotope dilution (U_ID) sample, label a new 14 mL PFA Teflon screw-top vial, transfer approximately 2 mL 1 M HNO_3 to vial, and obtain the weight of the vial. Add the desired amount of secondary dilution solution to vial, cap and weigh. Add the desired amount of ^{233}U spike to vial, cap and weigh. Place the vial on a hotplate, and heat at about 100°C to equilibrate.

6.3.3 For each thorium isotope dilution sample, label a new 14 mL PFA Teflon screw-top vial, transfer ca. 2 mL 1 M HNO_3 to vial, and obtain the weight of vial. Add the desired amount of Primary Solution to the vial, cap and weigh. Add the desired amount of ^{229}Th spike to vial, cap and weigh. Place the vial on a hotplate, and heat at about 100°C to equilibrate.

6.4 Uranium purification procedure.

6.4.1 Highly precise isotopic analyses by MC-ICPMS may be made from as little as 20 nanogram of U, so that only a small fraction of bulk uranium samples needs to be purified for mass spectrometry. For measurement of the uranium isotopic composition (U_IC), aliquot an appropriate amount of the primary sample solution, usually only a few microliters, into a 14 mL PFA vial.

6.4.2 Dry the U_IC aliquot and the U_ID aliquot from Step 6.3.2 on a hotplate; add 2 drops of conc. HNO_3 and dry again. Purify both of these aliquots using the following steps.

6.4.3 Prepare a 1.0 mL EiChrom UTEVA resin bed in a Bio-Rad Poly-Prep column. Check for and remove any air bubbles in the resin bed, and condition the resin bed with 2 mL of Milli-Q H_2O followed by 4 mL of 4 M HNO_3.

6.4.4 Dissolve the sample in 0.5 mL of 4 M HNO_3. Warm on a hotplate and cool in an ultrasonic bath. Load the sample onto the column. U adsorbs and most contaminants pass in the effluent. Rinse the resin with 0.5 mL then with 1 mL of 4 M HNO_3 passed through the vial.

6.4.5 Rinse the resin bed with 1mL and then 2 mL of 4 M HNO_3 loaded directly on the column.

6.4.6 Rinse the resin bed with 0.5 mL, and then 1 ml of 9 M HCl, and follow this with 5 mL of 5 M HCl loaded as 2 mL and then 3 mL. Rinse the Teflon vial that the sample was loaded from and position it under the column to catch the elution.

6.4.7 Elute U by adding 0.5 mL, 1 mL, 2 mL and then 3 mL of 0.1 M HCl. Dry the sample on a hotplate.

6.4.8 When the sample is dry, add 2 drops of concentrated HNO_3 and dry again. Repeat. The sample is ready to dissolve for MC-ICPMS analysis.

6.5 Thorium separation from bulk uranium

6.5.1 Dry the Th isotope dilution aliquot from Step 6.3.3 on a hotplate. Add 2-3 drops of concentrated HCl and dry. Dissolve the sample in 1 mL of 9 M HCl with 0.025 mL of concentrated HNO_3. Warm the sample on a hotplate and cool in an ultrasonic bath.

6.5.2 Prepare a 1.8 mL anion exchange resin bed (Bio-Rad AG1-X8, 100-200 mesh, chloride form) in a Bio-Rad Poly-Prep column. Check for and remove any air bubbles in resin bed. Condition the resin bed with 6 mL of 9 M HCl.

6.5.3 Label a new 14 mL PFA Teflon vial for Th fraction, and place this vial under the column.

6.5.4 Load the sample on the resin bed. U adsorbs on resin, and Th passes into vial beneath the column. Rinse the original sample vial with 1 mL of 9 M HCl and load this rinse on the column. Rinse the original sample vial again with 2 mL of 9 M HCl and load on the column. Rinse the resin bed with 2 mL, and then another 2 mL of 9 M HCl.

6.5.5 Dry the Th fraction on a hotplate. Add 2-3 drops of concentrated HNO_3 to the sample and dry. Repeat.

6.6 Thorium purification

6.6.1 Prepare a 1.0 mL anion exchange resin bed (Bio-Rad AG1-X8, 100-200 mesh, chloride form) in a Bio-Rad Poly-Prep column. Check for and remove any air bubbles in resin bed. Condition the resin bed with 6 mL of 8 M HNO_3.

6.6.2 Dissolve the Th sample in 0.5 mL of 8 M HNO_3. Warm the sample on a hotplate and cool in an ultrasonic bath.

6.6.3 Load the Th sample on the anion column. Rinse the sample vial with 1 mL, 1 mL, then 2 mL of 8 M HNO_3, loading each rinse solution on the column. Rinse the resin bed with an additional 2 mL of 8 M HNO_3.

6.6.4 Clean the sample vial, and place beneath the column to collect Th. Elute Th with 2 mL of 9 M HCl, followed by 1 mL, 2 mL, then 3 mL of 0.1 M HCl + 0.005 M HF. Dry the Th sample on a hotplate, add 2-3 drops of concentrated HCl and dry again.

6.7 Final thorium purification

6.7.1 Prepare a 1.0 mL anion exchange resin bed (Bio-Rad AG1-X8, 100-200 mesh, chloride form) in a Bio-Rad Poly-Prep column. Check for and remove any air bubbles in resin bed. Condition the resin bed with 5 mL of 9 M HCl.

6.7.2 Dissolve the Th sample in 0.5 mL 9 M HCl with 0.015 mL concentrated HNO_3. Warm the sample on a hotplate and cool in an ultrasonic bath. Label a new 14 mL vial for the Th fraction, and place this vial under the column.

6.7.3 Load the sample solution on resin bed. Rinse the sample vial with 1 mL and then another 1 mL of 9 M HCl, and load these rinses on the column. Rinse the resin bed with another 2 mL of 9 M HCl.

6.7.4 Dry the Th sample on a hotplate. Add 2-3 drops of concentrated HNO_3 and dry. The sample is ready to dissolve for mass spectrometry.

7 CALCULATIONS, DATA ANALYSIS AND REPORTING

7.1 Grams of sample per gram of solution.

7.1.1 The mass of sample per gram of primary solution is calculated by dividing the sample mass by the final mass of the primary solution. For a metal sample the mass is measured directly in step 6.1.3. The mass of an oxide sample is the mass of the quartz vial plus oxide from step 6.1.3 minus the initial mass of the quartz vial from step 6.1.2. The mass of the primary solution is the final mass of the vial plus solution measured in step 6.1.7 minus the initial mass of the vial measured in step 6.1.1.

7.1.2 The mass of sample per gram of secondary solution is calculated by dividing the sample mass in the primary solution aliquot taken for dilution by the final mass of the secondary solution . The mass of sample in the primary solution aliquot is determined by multiplying the mass of primary solution aliquot by the gram sample per gram solution calculated in step 7.1.1. The mass of the primary solution aliquot is determined by subtracting the mass of the PFA vial with 4 M HNO_3 from the mass of the vial containing 4 M HNO_3 and the primary solution aliquot, both measured in step 6.2.1. The mass of the secondary solution is the final mass of the bottle plus solution measured in step, minus the mass of the empty bottle, both measured in step 6.2.2.

7.1.3 The mass spectrometry analyses for uranium isotopic composition and the isotope dilution samples for U and Th are made using the procedure “Th and U Mass Spectrometry for ^{230}Th-^{234}U Age Dating”. Isotope concentrations are calculated from the isotope ratio results using Excel workbooks and reported according to customer specifications.

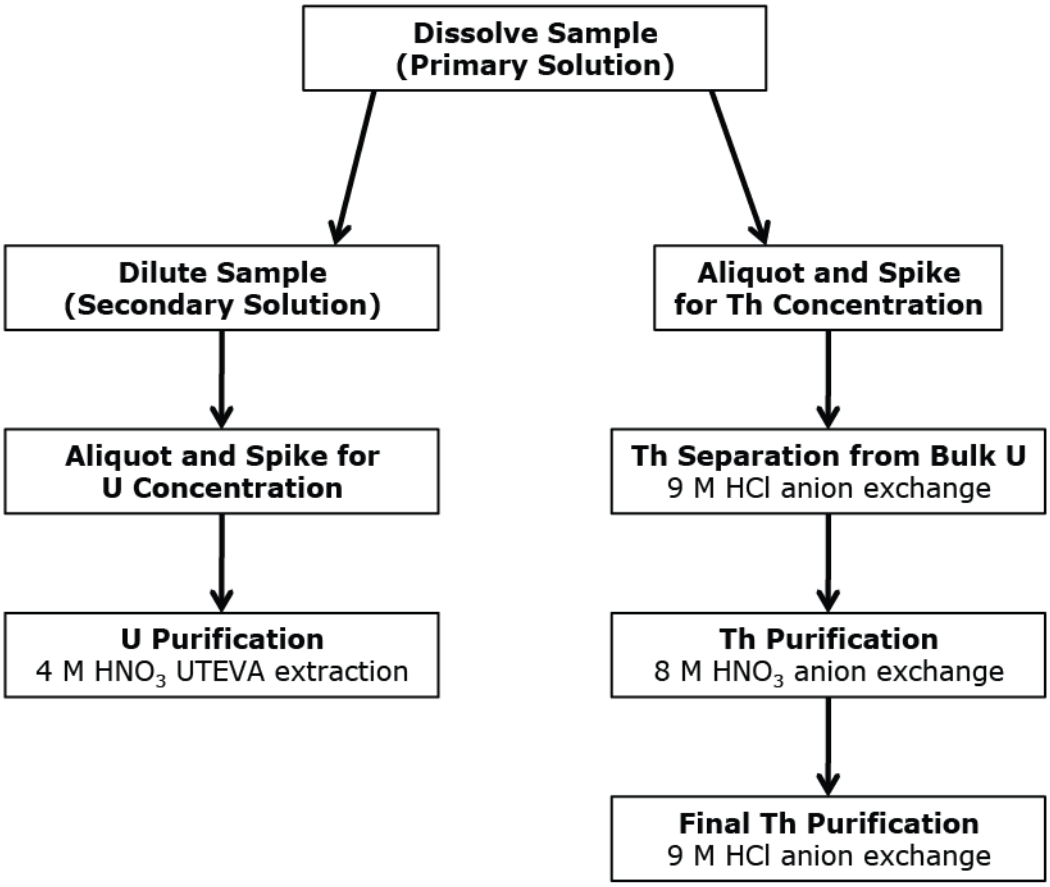
8 References

8.1 Dissolution: ASTM Method C1380-04 -- *Standard Test Method for the Determination of Uranium Content and Isotopic Composition by Isotope Dilution Mass Spectrometry*

8.2 Purification: Eichrom Technologies Inc. Analytical Procedures, ACS07 -- *Uranium in soil (2 grams sample)*

8.3 Williams, R. W. and Gaffney, A. M. *^{230}Th-^{234}U model ages of some uranium standard reference materials,* Proc. Radiochim. Acta 1, 31–35 (2011)

FLOWCHART OF ANALYTICAL PROCEDURE



Th and U Mass Spectrometry for ^{230}Th-^{234}U Age-Dating

1.0 SCOPE AND APPLICATION

This procedure describes the analysis of samples of thorium and uranium for isotopic composition by multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). The MC-ICPMS instrument is a NuPlasma HR manufactured by Nu Instruments, Ltd. Both spiked and un-spiked samples of uranium are analyzed, from which U concentration and isotopic composition are calculated. The uranium spike isotope is ^{233}U and the thorium spike isotope is ^{229}Th. This procedure is applicable to samples of uranium and thorium that have been highly purified from other elements and from each other. While no minimum sample size is specified, the sensitivity of the NuPlasma is sufficient to make isotopic analyses of 1 nanogram of uranium and less than 1 picogram of thorium.

2.0 SUMMARY OF METHOD

Uranium and thorium samples, dissolved in 2% nitric acid (vol/vol) and 2% nitric acid + 0.005 M hydrofluoric acid, respectively, are nebulized and transported as aerosol with argon carrier gas to the ICP torch. The NuPlasma has an array of eleven Faraday cup collectors, and three electron multiplier pulse-counting detectors. Two of the pulse-counters have energy filters to improve the abundance sensitivity (reduce the effects of tailing and scattered ions). Whenever possible, multiple detectors are used to measure isotopic composition by simultaneously collecting the ion beams from the different isotopes. Ion beam currents are generally integrated for a total of 100 to 300 seconds, and are recorded as 20 or 30 separate integrations (cycles) of 5 or 10 seconds each. Background is measured on a blank solution of 2% nitric acid (or 2% nitric + 0.005 M hydrofluoric acid, for thorium) prior to sample analysis, and uranium standards are measured to determine the mass bias correction and any necessary detector cross-calibration factors (gain factors). The sample data are corrected by baseline and background subtraction and for detector gains. Cycle by cycle ratios are calculated and then corrected for mass bias.

3.0 INTERFERENCES AND LIMITATIONS

3.1 SAMPLE MATRIX

Samples for the MC-ICPMS must be especially pure, as microgram levels of common matrix elements like Ca and Fe can affect the instrumental mass bias. The mass bias correction factors determined on pure standard solutions may not accurately reflect the actual mass bias for contaminated samples.

3.2 HYDRIDES, ARGIDES, OXIDES and OTHER CLUSTERS

Hydrides and oxides (single hydrogen and single oxygen additions to metal ions), with +1 charge are formed in the ICP torch from the air and water introduced with the sample. Oxide interferences with uranium and thorium isotopes are

essentially non-existent, but other cluster ions are possible in samples that are contaminated with platinum or lead. These potential interference clusters are given in the following table, but Pt and Pb are generally well-separated during purification.

Isotope	Potential Interference Clusters
230Th	16O-16O-198Pt
234U	40Ar-194Pt
234U	14N-14N-206Pb
235U	40Ar-195Pt
235U	1H-40Ar-194Pt
235U	14N-14N-207Pb
238U	40Ar-198Pt
238U	14N-16O-208Pb
238U	16O-16O-206Pb

Hydrides, on the other hand, are more common. For example, both ^{229}Th-H on ^{230}Th, and ^{233}U-H on ^{234}U, are present at the 3-5 ppm level. For most samples, corrections for hydride formation are insignificant.

4.0 APPARATUS AND MATERIALS

4.1 NuPlasma HR multi-collector ICP-MS (Nu Instruments, Ltd.).
4.2 Cetac Aridus II sample introduction system (Cetac Instruments, Inc.).
4.3 Cetac ASX-112 autosampler (Cetac Instruments, Inc.).
4.4. Polyethylene sample cups, 2.0 ml capacity (Cetac Instruments, Inc.).

5.0 ANALYTICAL REAGENTS

5.1 2% nitric acid (vol/vol) prepared from Seastar concentrated nitric acid and ASTM Type II reagent grade water (Seastar Chemical Co.; Milli-Q water, 18 Mohms).
5.2 2% nitric acid (vol/vol) + 0.005 M hydrofluoric acid prepared from Seastar. Concentrated acids and ASTM Type II reagent grade water (Seastar Chemical Co.; Milli-Q water, 18 Mohms).
5.3 Uranium standard solution in 2% nitric acid, about 10-15 ppb, prepared from NBL U010 uranium oxide standard. This standard solution is used to determine the mass bias and relative detector gain factors.
5.4 Isotopic uranium quality control (QC) solutions. These solutions are either prepared from the original NBS materials, or they are prepared from materials issued by New Brunswick Laboratory (NBL CRMs). Routinely, solutions of both CRM 129A and U005-A, are used for QC check standards.
5.5 Isotopic thorium QC solution. An in-house standard solution that is approximately equal atom ^{229}Th-^{230}Th-^{232}Th is used as a QC check solution.

6.0 PROCEDURE

6.1 Instrument Operation.
Operation of the NuPlasma and acquisition of accurate isotopic composition data requires both a high level of expertise in inorganic mass spectrometry and extensive experience with the instrument itself. That level of expertise and experience is assumed.

6.2 Uranium Isotopic Analyses.

6.2.1 Purified samples for isotopic uranium analyses are dissolved in 3 mL of 2 % nitric acid.

6.2.2 Although estimates of the uranium content of the samples are generally available, additional dilutions of the sample solutions are prepared in 2 mL polyethylene auto-sampler vials. Generally, 100-fold or 1000-fold dilutions are prepared for initial testing to ensure that the concentration of uranium in the solution introduced to the NuPlasma is less than about 20 ppb. Using readings of the uranium beam intensities from these test solutions, dilutions of the sample are prepared which will give beam intensities of 4 to 7 volts for the most abundant uranium isotope, usually ^{238}U.

6.2.3 QC check samples are prepared to give ^{238}U beam intensities in the range of 4 to 7 volts.

6.2.4 Data acquisition programs are selected or created specifically for collection of isotope ratio data using simultaneous multi-collection techniques wherever possible. Generally, Faraday cups are used to determine the intensities of beams from ^{233}U, ^{235}U and ^{238}U and the pulse-counting detectors are used to measure the lower intensity beams from ^{234}U and ^{236}U.

6.2.5 Analyses of 2 % nitric acid using the same data acquisition programs that are used for the sample analysis are made before each sample and subtracted from the sample peak intensities.

6.2.6 Analyses of the uranium standard (U010) are made at the beginning and end of each batch of samples. U010 is also analyzed periodically within the batch, and no more than eight samples are ever analyzed consecutively between analyses of this CRM. The certified $^{238}U/^{235}U$ atom ratio for this CRM is used to determine the instrumental mass bias. A formulation of the exponential mass fractionation law is used to calculate average mass bias correction factors for each measured ratio. Corrected isotope ratios are calculated by multiplying the measured ratio by these average correction factors.

6.2.7 The U010 analyses are also used to determine the detector cross-calibration factor for the pulse-counters relative to the Faraday detector. These gain factors are determined using the ^{234}U and ^{236}U beams on the pulse-counters relative to the ^{235}U beam on the Faraday detector measured simultaneously.

6.2.8 Unknown samples are analyzed using the selected data acquisition programs. Between sample analyses, a rinse of the sample inlet system is accomplished by introduction of 5% and then 2% nitric acid for several minutes each. The rinse-out time required to reduce the carry-over signal from the previous

sample to blank levels will depend on the sample signal intensities. This time is determined during set up and incorporated in the analytical protocol. The effectiveness of the rinse-out is determined by measuring the blank intensities as called for in Step 6.2.5.

6.2.9 Standard reference materials for isotopic uranium are analyzed using the same data acquisition programs as for the samples. At least one of these QC check samples is analyzed for each batch of samples, and no more than eight unknown samples are analyzed before or between the QC check analyses.

6.3 Thorium Isotopic Analyses.

6.3.1 Samples for isotopic thorium analyses are dissolved in 3 mL of 2 % nitric acid + 0.005 M hydrofluoric acid.

6.3.2 Test dilutions of the Th sample solutions are prepared in 2 mL polyethylene auto-sampler vials. Generally, 10-fold dilutions are prepared for initial testing to ensure that the concentration of thorium isotopes in the solution introduced to the NuPlasma is less than about 10 ppb. Using readings of the thorium beam intensities from these test solutions, the data acquisition strategy will be determined. Simultaneous Faraday multi-collection of all Th isotopes is sometimes possible. More commonly, ^{229}Th and ^{230}Th will be analyzed with pulse-counting detectors, with ^{232}Th on either a Faraday cup or a pulse counter. Dilutions of the sample are prepared, if necessary, which will give the maximum beam intensities for Th, but no more than about 6 volts for the most abundant isotope; generally ^{232}Th.

6.3.3 Because Th concentrations are often limited and because high precision isotope ratios depend on maximizing the beam intensities, it is often the case that Th samples will be analyzed using the original 3 mL dilution. This dilution provides enough volume to repeat the analysis at least one more time, if necessary.

6.3.4 Data acquisition programs for Th have been created specifically for collection of isotope ratio data using simultaneous multi-collection techniques wherever possible. Working with the beam intensities in the dilutions, three different data acquisition techniques are most common. From lowest to highest intensity these are: (1) simultaneous pulse-counting of all isotopes; (2) simultaneous Faraday/pulse-counting, where only the major isotope, generally ^{232}Th, is analyzed with the Faraday detector; and (3) simultaneous Faraday multi-collection. Simultaneous Faraday/pulse-counting with peak jumping is also quite useful.

6.3.5 Dilutions of the in-house Th QC check sample are prepared at appropriate concentrations to match the beam intensities of the samples.

6.3.6 Analyses of 2 % nitric acid + 0.005 M HF using the same data acquisition programs that are used for the sample analysis are made before each sample and subtracted from the sample peak intensities.

6.3.7 As for uranium, analyses of U010 are made, at minimum, at the beginning and end of each batch of samples to determine the instrumental mass bias

and the detector cross-calibration factors for the pulse-counting detectors relative to the Faraday array (steps 6.2.6 and 6.2.7).

6.3.9 Unknown samples are analyzed using the selected data acquisition programs. Between sample analyses, a rinse of the sample inlet system is accomplished by introduction of 5% nitric acid + 0.01 M HF followed by 2% nitric acid + 0.005 M HF solution for several minutes each. The rinse-out time required to reduce the carry-over signal from the previous sample to blank levels will depend on the sample signal intensities. This time is determined during set-up and incorporated in the analytical protocol. The effectiveness of the rinse-out is determined by measuring the blank intensities as called for in Step 6.3.6.

6.3.10 The in-house Th-standard solution is analyzed using the same data acquisition programs as for the samples. The measured Th isotopic composition is compared against historical results as a check of the relative detector gain calibration. At least one of these QC check samples is analyzed for each batch of samples, and no more than eight unknown samples are analyzed before or between the QC check analyses.

7.0 CALCULATIONS, DATA ANALYSIS AND REPORTING

7.1 Isotope ratio data are calculated from the beam intensity data in three steps. First, the baseline-corrected raw intensities are corrected by subtracting background intensities as measured on the blank solutions, and are then corrected by multiplying by the appropriate relative detector gain factors. Second, the required ratios are calculated; and third, the ratios are corrected for instrumental mass bias. Uncertainties on these ratios are calculated from the standard error on the mean of the replicate ratio analyses (n = number of cycles), the dispersion on the replicate determination of the detector gain factors, the certified value of the standard used for mass bias correction, and an estimate of the uncertainty due to blank subtraction obtained from counting statistics.

The baseline, blank, and gain-corrected isotope ratios are corrected for instrumental mass bias using the exponential mass fractionation law as follows:

$$R_{Corrected}^{x/y} = R_{Measured}^{x/y}\left(mass_x / mass_y\right)^{\beta}$$

where R is the atomic ratio of isotope *x* to isotope *y*, and $mass_x/mass_y$ is the ratio of their atomic weights. The exponential factor, β, is determined from analyses of standards.

$$\beta = \frac{\ln\left(R^{a/b}_{Standard} / R^{a/b}_{Measured}\right)}{\ln\left(mass_a / mass_b\right)}$$

Where the atomic ratio of isotope *a* to isotope *b* in the standard is the known or accepted value.

7.2 From the isotope ratio results for $^{234}U/^{233}U$ and $^{230}Th/^{229}Th$, the concentration of ^{234}U and ^{230}Th are calculated using standard isotope dilution equations. The results may be expressed in units of (atoms/g-Primary Solution) or (atoms/g-sample) if the (g-sample/g-Primary Solution) is known.

7.3 The age of the sample is determined using the simplified age-dating equation

$$t = \frac{1}{(\lambda_1 - \lambda_2)} ln\left[1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}\right]$$

where R is the $^{230}Th/^{234}U$ atomic ratio, and λ_1 and λ_2 are the decay constants of ^{234}U and ^{230}Th, respectively. The values used at LLNL for these decay constants are from Cheng *et al*. "The half-lives of uranium-234 and thorium-230", Chemical Geology 169 (2000) 17–33.

	230Th	234U
Half-life (years)	7.569E+04	2.4525E+05
Std uncertainty (years)	115	245
Decay Constants (per year)	9.15771E-06	2.82629E-06
Std uncertainty	1.39E-08	2.82E-09

7.1.4 The combined standard uncertainty on the age (t) is the square-root of the following expression

$$u(t)^2 = \left(u(\lambda_1)\frac{\partial t}{\partial \lambda_1}\right)^2 + \left(u(\lambda_2)\frac{\partial t}{\partial \lambda_2}\right)^2 + \left(u(R)\frac{\partial t}{\partial R}\right)^2$$

where the sensitivity coefficients are

$$\frac{\partial t}{\partial R} = \frac{1}{\lambda_1 + R(\lambda_1 - \lambda_2)}$$

$$\frac{\partial t}{\partial \lambda_1} = \left(\frac{1}{\lambda_1 - \lambda_2}\right)\left(\frac{1}{1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}}\right)\left(\frac{\lambda_2 R}{{\lambda_1}^2}\right) - \frac{1}{(\lambda_1 - \lambda_2)^2} ln\left(1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}\right)$$

$$\frac{\partial t}{\partial \lambda_2} = \frac{1}{(\lambda_1 - \lambda_2)^2} \ln\left(1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}\right) - \frac{R}{\lambda_1(\lambda_1 - \lambda_2)\left(1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}\right)}$$